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Phase Mixed Polyurethane Synthesis

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Defence Research Establishment Atlantic

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Abstract

The use of Group Contribution Analysis (GCA) and Group Interaction Modelling (GIM) to model the dynamic mechanical properties of polymers is the subject of an ongoing TTCP (The Technical Cooperation Panel) study. This report describes the synthesis of 20 phase mixed thermoplastic polyurethanes that will be characterized and modelled by GCA and GIM. The polyurethane formulations were synthesized from 4,4'-methylenebis(phenyl isocyanate) or 1,6-diisocyanatohexane, and glycol, polgylcol, or glycol/polyglycol mixtures. The standard "one-shot" batch reaction method was initially tried for several of the formulations, but a number of problems were identified. These included bubble formation in the samples, high exotherms, and fast reaction times. As a result, a solution polymerization/ solution casting method was developed, using N,N-dimethylformamide as a solvent. This approach has several advantages including control of the reaction temperature and rate and the absence of bubble formation in the samples. All 20 of the formulations were successfully prepared in solution, and 15 of the formulations were successfully solvent cast into 1 mm thick film samples for DMTA testing. Five of the samples did not form satisfactory films on solvent evaporation, as a result of cracking or non-uniform geometries that developed during the drying process. Gel permeation chromatography experiments revealed the presence of 1- 3% low molecular weight species which was attributed to oligomer content in polyurethanes prepared from 2,2-dimethyl-1,3-propanediol chain extender. Elemental analysis results were on average within 1.32%, 0.40%, 0.50%. and 1.91% of their expected values for carbon, hydrogen, nitrogen, and oxygen, respectively.

Résumé

L'utilisation de l'analyse par contribution de groupe (ACG) et de la modélisation de l'interaction de groupe (MIG) pour modéliser les propriétés mécaniques dynamiques de polymères est le sujet d'une étude en cours du Comité de coopération technique (CCT). Ce rapport décrit la synthèse de 20 polyuréthanes thermoplastiques en phase mixte qui seront caractérisés et modélisés grâce à l'ACG et à la MIG. Les préparations de polyuréthane ont été synthétisées à partir de 4,4'-méthylènebis(isocyanate de phényle), ou de 1,6-diisocyanatohexane, et de glycol, de polyglycol ou de mélanges de glycol/polyglycol. On a d'abord utilisé la méthode classique « d'un coup » en à un lot pour synthétiser plusieurs des préparations, mais un certain nombre de problèmes ont alors été identifiés, dont la formation de bulles dans les échantillons, le dégagement d'une grande quantité de chaleur et de courts temps de réaction. En conséquence, on a mis au point une méthode de polymérisation en solution/moulage en solution comportant l'utilisation de N,N-diméthylformamide comme solvant. Cette approche présente plusieurs avantages dont la régulation de la température et de la vitesse de réaction et l'absence de bulles dans les échantillons. On a préparé les 20 préparations en solution et on a moulé en solvant 15 d'entre elles pour obtenir des échantillons de film de 1 mm d'épaisseur qui ont été soumis à l'analyse thermique mécanique dynamique. Dans le cas de cinq des échantillons, l'évaporation du solvant n'a pas donné des films satisfaisants en raison des fissures et des formes irrégulières qui sont apparues durant le séchage. L'analyse par chromatographie par perméation de gel a révélé la présence de 1 à 3 % d'espèces de faible poids moléculaire, ce qui a été attribué à la teneur en oligomère des polyuréthanes préparés à partir de 2,2-diméthyl-1,3-propanediol qui était utilisé

comme allongeur de chaîne. L'analyse élémentaire donne des valeurs qui se situent en moyenne à 1,32, 0,40, 0,50 et 1,91 % des valeurs prévues respectivement pour le carbone, l'hydrogène, l'azote et l'oxygène.

DREA CR 2000-076

Phase Mixed Polyurethane Synthesis
D. Cook

EXECUTIVE SUMMARY

Background
DREA is involved in a TTCP study (MAT-TP6-O9) whose goal is to validate and extend models which relate the dynamic mechanical properties of polymers to their chemical structure. Group Contribution Analysis (GCA) has been used extensively as an empirical tool for predicting many polymer properties, such as density, glass transition temperature, dielectric constant, refractive index, and the elastic modulus. The relationship of viscoelastic properties to the chemical structure of polymers has received less attention, but is important in the optimized design and development of engine mounts, anechoic coatings, and decoupling tiles for defence applications. A specific goal of the TTCP project is to investigate the possibility of predicting the height, width, and frequency of the mechanical loss peak from the chemical structure of the polymer. This report details the work undertaken to synthesize a series of 20 polyurethanes to be used in the TTCP study.

Principal Results
About half of the 20 formulations were synthesized using the conventional synthesis procedure. This involved melting and degassing the reactants separately, mixing the reactants in the reaction vessel, and casting the partially polymerized urethanes into a mold, where the polymerization reaction was taken to completion. Problems with this approach included (a) solubility and volatility of reactants; (b) fast reaction times/ high exotherms, which prevented transfer to mold; and (c) the appearance of bubbles in some cases. To avoid these problems, a solution polymerization approach was investigated. Reactants were dissolved in a solvent, reacted, and then cast onto a plate, where the solvent was evaporated. All 20 formulations were prepared in solution, and 15 of the formulations were successfully cast into bubble-free films of roughly 1 mm thickness.

Significance of Results
This work represents a major milestone in the TTCP Operating Assignment. Synthesis of the polyurethanes was the first step in the GCA study. The solution polymerization approach was found to have several advantages over the conventional one-shot method that is usually used for thermoplastic polyether polyurethanes:

- Solvent reacted/ cast samples did not have bubbles.
- The reaction temperature could be controlled, and there was no problem with exotherms.
- Problems with reactant miscibility were avoided.

Future Work

Suitable samples for 5 of the formulations need to be prepared through a modified casting procedure. The next step in this work is to characterize the polyurethane samples using dynamic mechanical analysis, followed by group contribution analysis of the experimental data.

J. Szabo, Scientific Authority
June 2000

CRDA CR 2000-076

Synthèse de polyuréthane en phase mixte
D. Cook

RÉSUMÉ

Contexte
Le CRDA participe à une étude du CCT (MAT-TP6-O9) dont l'objectif est de valider et d'extrapoler des modèles qui mettent en relation les propriétés mécaniques dynamiques des polymères et leur structure chimique. L'analyse par contribution de groupe (ACG) a été largement utilisée comme méthode empirique pour prévoir de nombreuses propriétés des polymères, telles que la masse volumique, la température de transition vitreuse, la constante diélectrique, l'indice de réfraction et le module d'élasticité. Malgré son importance pour l'optimisation de la conception et la mise au point de bâtis moteurs, de revêtements anéchoïdes et de tuiles de découplage pour des applications militaires, la relation entre les propriétés viscoélastiques et la structure chimique des polymères a fait l'objet d'une étude moins approfondie. L'un des objectifs spécifiques du projet du CCT est d'étudier la possibilité de prévoir la hauteur, la largeur et la fréquence du pic de perte mécanique à partir de la structure chimique du polymère. Ce rapport décrit en détails les travaux entrepris pour synthétiser une série de 20 polyuréthanes qui seront utilisés lors de l'étude du CCT.

Principaux résultats
Environ la moitié des 20 préparations ont été synthétisées à l'aide de la méthode classique qui comprenait la fusion et le dégazage séparés des réactifs, le mélange dans le réacteur, puis le moulage des uréthanes partiellement polymérisés dans un moule où la réaction de polymérisation était complétée. Parmi les problèmes que comportait cette approche, on compte : a) la solubilité et la volatilité des réactifs; b) les courts temps de réaction et le dégagement d'une grande quantité de chaleur, ce qui empêchait le transfert dans le moule, et c) l'apparition de bulles dans certains cas. Pour éviter ces problèmes, nous avons étudié une approche par polymérisation en solution. On dissout les réactifs dans un solvant, on les fait réagir, puis on coule le mélange sur une plaque où le solvant s'évapore. Les 20 préparations ont été préparées en solution, et on a réussi, avec 15 d'entre elles, à obtenir un film d'environ 1 mm d'épaisseur, exempt de bulles.

Importance des résultats
Ces travaux constituent une étape importante de la mission du CCT. La synthèse des polyuréthanes représentait la première étape de l'étude par ACG. On a constaté que l'approche par polymérisation possède plusieurs avantages par rapport à la méthode classique « d'un coup » normalement utilisée pour synthétiser des polyéthers-polyuréthanes thermoplastiques :

- les échantillons synthétisés dans un solvant puis moulés ne renferment pas de bulles.
- la température de la réaction peut être régulée et le dégagement de chaleur ne constitue pas un problème.
- on évite les problèmes liés à la miscibilité des réactifs.

Travaux futurs

Des échantillons acceptables de cinq des préparations devront être préparés grâce à une procédure modifiée de moulage. La prochaine étape de ces travaux comprendra la caractérisation d'échantillons de polyuréthane, d'abord par analyse mécanique dynamique, puis par analyse de contribution de groupe des données expérimentales.

J. Szabo, responsable scientifique
Juin 2000

1.0 INTRODUCTION

Defense Research Establishment Atlantic (DREA) is involved in a Technical Cooperation Program (TTCP) study with the goal of predicting the dynamic mechanical properties of a set of thermoplastic polyurethanes from their chemical structures using methods such as Group Contribution Analysis (GCA) and Group Interaction Modeling (GIM)[1,2]. To carry out this program a set of 20 phase-mixed thermoplastic polyurethanes of varying composition were selected for synthesis. Results from analysis of these materials would then be used to refine the GCA and GIM models.

In this project the synthesis of these polyurethanes was carried out with the intent of making 1.5 mm and 3.0 mm thick plaques and 0.25" x 0.25" x 8" bars for testing.

2.0 MATERIALS

The matrix of polyurethane formulations selected for synthesis is shown by stoichiometry in Table A1 and by mass percent composition in Table A2 (see Appendix A). Specific suppliers and grades were requested for the monomers; these were procured and are listed below:

Table I
Materials

Acronym	Chemical	Supplier	Product	Amount procured
BDO	1,4-butanediol	Aldrich Chemical	cat.# 24,055-9	6 x 100 g
DEG	di(ethylene glycol)	Aldrich Chemical	cat.# H2,645-6	4 kg
DMPD	2,2-dimethyl-1,3-propanediol	Aldrich Chemical	cat.# 12,658-6	3 kg
T650	poly(tetramethylene ether glycol) MW=650	Dupont	Terathane 650	~ 1 gallon
T1000	poly(tetramethylene ether glycol) MW=1000	Dupont	Terathane 1000	~ 1 gallon
T1400	poly(tetramethylene ether glycol) MW=1400	Dupont	Terathane 1400	~ 1 gallon
P600	poly(ethylene glycol) MW=600	Union Carbide	Carbowax 600	1 kg
P1000	poly(ethylene glycol) MW=1000	Union Carbide	Carbowax 1000	1 kg
MDI	4,4'-methylenebis(phenyl isocyanate)	Bayer	Mondur M	5 kg
HDI	1,6-diisocyanatohexane	Bayer	Desmodur H	1 kg

[1] J.P. Szabo, *Polymers For Noise Reduction in Military Platforms*, TTCP PTP-6-O9 Operating Assignment Report, published in TTCP MAT Panel 6 Annual Report, December 1998.
[2] J.P Szabo, *Acoustic Damping in Polymers*, TTCP Study Assignement, PTP-6-S2/ (PTP-3-S11), December 1996.

Prior to use, the BDO and DEG liquids were stored over activated molecular sieves (Aldrich cat# 33,430-8 : 4Å, 1.6 mm pellets) for further drying. The polyols and DMPD were used as received.

Number average molecular weights of the polyether materials were obtained from lot analysis data provided by resin manufacturers. End group titration is used, wherein -OHs at the end of the individual polymer chains are titrated to generate a "hydroxyl number" (i.e. mg KOH/g of polymer). Since the polymer is bifunctional (i.e. 2 -OHs per polymer chain), the number average molecular weight can be calculated and is shown in Table II.

Table II
Number Average Molecular Weight (M_n) for Supplied Polyether Lots

Manufacturer	Polyether Type and Grade	Lot #	Hydroxyl Number	Number Average mol. wt. (M_n)
DuPont	T650	L65110823	175 72	639*
	T1000	L10120725	114 7	978*
	T1400	L1471102L	81 54	1376*
Union Carbide	P600	0000275786	not given	590
	P1000	0000101980	not given	982

*calculated from hydroxyl number

Typical molecular weight distribution data for each polyether grade was also obtained from the manufacturers. This analysis is not done routinely on a lot basis, but representatives of DuPont and Union Carbide indicated the distributions can safely be assumed to be representative of the lots supplied. Typically, variations in the production process will shift the molecular weight (which would be seen in the M_n value) but the MW distribution will remain relatively invariant.

Table III
Typical Molecular Weight Distribution for Polyether Grades

Manufacturer	Polyether Type and Grade	Analytical * Method Used	M_n	M_w	M_z	M_w/M_n	M_z/M_w
DuPont	T650	GPC	703	1230	1950	1.750	1.585
	T1000	GPC	1040	1710	2590	1.644	1.515
	T1400	GPC	1467	2569	3914	1 751	1.524
Union Carbide	P600	GC	570	589	607	1 033	1 031
	P1000	LC	978	1014	1047	1.037	1 033

* GPC = gel permeation chromatography, LC = liquid chromatography

3.0 "ONE-SHOT" BATCH REACTION METHOD

Naval Surface Warfare Center (NSWC) was successful in preparing a few of the polyurethane samples by a "one-shot" procedure in which the polyols/glycols and isocyanates were intensively mixed for 2 minutes in a Ross mixer and then injected into aluminum molds[3]. Not all of the reactions had been attempted, however.

It was noted that the compositions given in Table A1 had the potential to react in a radically different manner from one another and some of the most difficult had not been attempted. While we considered the "one-shot" method to be the best procedure for preparation of thermoplastic polyurethanes, it was unclear whether the method could be extended to include all of the reactions. Therefore, the most difficult, fast reactions were attempted using this method with the expectation that any reaction conditions derived could be extended to the slower, less demanding reactions.

3.1 Initial Polymerizations

After a few familiarization runs, the following procedure was used for the initial polyurethane polymerizations:

1. Polyether and/or glycol materials were weighed into a glass reaction vessel (screw top 500 mL jar) and the vessel was placed in a heated oil bath. The material was stirred using a marine-type propeller stirrer while the overhead space of the vessel was purged with a low flow of dry nitrogen.

2. Once all the polyether/glycol components were melted or dissolved, previously weighed out solid MDI was added to the mix and stirring continued. Polyethers and MDI are not mutually soluble and a semi-opaque two phase mix formed initially after the MDI melted. Stirring was continued for long enough that a clear mixture was observed, indicating a full compatibilization of the materials.

3. Once a clear mixture was observed, the reacting mass was dumped onto an aluminum pan with a PTFE liner. The pan was placed in a 60°C or 100°C forced air, vented oven for at least 4 hours to complete the cure.

It was found that the fastest reacting mixtures (e.g. DREA reactions #1, 1R, 13 and 13R) would polymerize very quickly to form a stiff polymer mass. Therefore, the reacting mixtures were dumped into lined aluminum pans as there was not enough time to transfer to the molds. The reaction also generated a great deal of heat during polymerization, causing an even faster reaction. Effective heat removal is required to control this "runaway" polymerization, but as the mixture becomes more viscous it is impossible to remove the heat quickly enough. It was determined that 50-55°C was the highest temperature that could be used initially. This was high enough to melt the MDI and any of the polyols, yet not so high as to cause an even faster polymerization reaction.

[3] Personal communication, Jeff Fedderly, NSWC, January 2000.

It was also noted that polyols and isocyanates were not totally miscible and a two layer mixture was formed initially on melting. Stirring continued until some clearing was seen, indicating a homogeneous solution had been formed. If the mixing was stopped before this time the phases would separate. The time to clearing depending on the reaction formulation and varied from under a minute to more than ½ hour. The fastest reacting mixtures cleared quickly and after clearing there were no more than 5 to 10 seconds before the material had set up completely. This was insufficient to transfer into the molds. Even for slower reactions, the viscosity increased rapidly making transfer of the polymer from the reaction vessel difficult.

It was also noted that there was a tendency for formation of bubbles in the polyurethane mass during curing. It was thought that this problem could be eliminated by vacuum degassing of the monomers *if* the problem of a too fast reaction could be avoided.

3.2 Compression Molding Trials

The pan-cure method was chosen when it was apparent that there was not enough time to transfer the reaction mixture into the molds before it began to set up. A second option was pursued in which the polyurethane was broken up and compression molded into the final desired shapes. This has the additional benefit of removal of residual stress in the formed samples.

Aluminum compression molds were made and molding tests carried out. It was soon found, however, that there were two major problems with this method:

1 Some of the polyurethanes could not be compression molded at reasonable temperatures. Molding temperature could be varied up to 180°C but even this temperature was not high enough for some materials to flow. DREA calculated the expected glass transition temperatures for the materials through the group contribution method and extrapolated melting temperatures based on these (see Table A3 in Appendix A)[4]. It was found that the T_m for reactions #1 and #13 would be well in excess of the decomposition temperature of the polyurethanes (~190°C). This was confirmed by DSC measurements. Therefore, these polyurethanes could not be compression molded.

[4] Personal communication, Jeff Szabo, DREA, February 2000

2. Although the other reaction materials could be molded at lower temperatures it was also found that residual bubbles within the melt could not be eliminated. This was unexpected. With the standard molding technique and mold design used it should have been possible to squeeze out the bubbles during molding. It was subsequently discovered that on heating, bubbles would *appear* and grow within the polyurethane melts. It was also found that an elastomeric 1/4" x 1/4" bar, which was essentially clear after initial compression molding, had numerous small dispersed bubbles appear throughout the section after sitting several days at room temperature.

It was not entirely clear why it was happening and a resolution to this last problem was never found.

3.3 Further Batch Trials

After further discussion between DREA and Bodycote Ortech it was agreed that the "one-shot" mixing and transfer to the mold procedure would be used to prepare as many samples as possible. It was understood that this procedure would not work with the fastest reacting mixtures. We would also attempt to follow NSWC's procedure as much as possible considering differences in equipment (NSWC used a Ross mixer, whereas we used a simple glass reaction vessel with stirrer). It was also noted that NSWC used a two minute intensive mixing time with all of the formulations and then transferred the mixture to the molds. We had used a variable mixing time, dependent on when the mixture cleared.

The following procedure was used for DREA reaction #5, which was an intermediate reaction rate formulation:

1. The required T1400 polyether was weighed into a 500 mL glass reaction jar and the vacuum cover (PTFE seal) screwed on.

2. The jar was placed into a 56°C water bath, heated, and a full vacuum drawn. The jar was swirled occasionally as the polyether started to melt.

3. At the same time MDI was weighed into a 250 mL RB flask, put under vacuum and then back-filled with nitrogen. The flask was heated using a heating mantle in order to melt the MDI.

4. Once the T1400 was completely melted, DMPD was added. The reactor was evacuated by vacuum and the back-filled with nitrogen.

5. Once all of the DMPD had dissolved in the T1400 polyol, the molten MDI was added and the material was rapidly mixed for two minutes under a nitrogen pad.

6. The mixture was then put under vacuum for two minutes to degas and then transferred to the dispensing gun. The aluminum molds, which had been previously coated with a release agent (Synair Synlube 1000 Release Agent), were then filled.

7. Once the molds were filled they were transferred to 70°C forced-air, ventilated ovens for overnight curing.

It was found that, while there was no difficulty in getting the polyurethane into the molds, problems with bubble formation continued. Bubbles would not be present initially but would appear after curing.

4.0 SOLUTION POLYMERIZATION METHOD

It was suggested that one way to solve many of the problems in making the polyurethanes would be to solution polymerize the polyurethane and then recover the polymer by solvent evaporation. Initial polymerizations of DREA reactions #1 and #5 in N,N-dimethyl formamide (DMF) solvent were successful in making the polymers without any problems with excessive heat buildup. Simple film castings made from the solutions were free of bubbling and other defects, although problems existed in trying to make films from reaction # 1 as there was a tendency for the dried films to "mud-crack" because they were so brittle.

In conjunction with DREA it was agreed that we would perform solution polymerizations of all the formulations and then cast the resulting solutions to give films with a thickness of at least 0.5 mm.

The following procedure was used for the solution polymerization at 40 w/w % in anhydrous DMF solvent:

1. Weigh out polyols and/or glycols with about 225 grams of anhydrous DMF (Caledon Laboratories, Cat# 3803-2-29) into a 500 mL jar. Heat mixture at 50°C in an oven, shaking occasionally to dissolve. After the polyols/glycols are completely dissolved pour solution into a 1 litre reaction kettle with a four-necked cover maintained in a water bath at 60-62°C. Stir at 80 to 100 rpm and purge solution by slowly bubbling in dry nitrogen for at least 20 minutes.

2. At the same time, weigh out required isocyanate into a 1 litre jar and add the remaining anhydrous DMF. Dissolve isocyanate by swirling the jar occasionally as required.

3. Once nitrogen purging of the polyol/glycol solution is complete and isocyanate is dissolved, add isocyanate solution to the stirring polyol solution using a drop funnel. For the fastest reactions the isocyanate solution is added over periods of up to one hour in order to minimize reaction exotherms, while for slower reactions the isocyanate solution can be added over 10 to 30 minutes.

4. After isocyanate addition, continue stirring for at least eighteen hours at 60-65°C. A dry nitrogen blanket is maintained above the polymerizing solution at all times.

5. After at least eighteen hours turn off the heat, allow solution to cool to room temperature and transfer to 1 litre bottles.

Initially, it was planned that 40 w/w% solutions would be made, but it became evident that some polymers would not be soluble at this concentration. Therefore, these polymers were prepared at 25% or even 20% non-volatile content (w/w). A summary of the properties of the polyurethane solutions is shown below.

Table IV
Properties of Polyurethane in DMF solutions

DREA Reaction #	Bodycote Ortech Sample Number	Wt % Non-Volatile in Solution	Relative Viscosity	Solution Colour	Precipitated?
1	00-05-8330-7	25	Very high	Yellow	No
1R	00-05-8330-8	25	Very high	Slightly yellow	No
2	00-05-8227-80	40	Low	White	Yes
3	00-05-8227-92	40	High	Slightly yellow	No
4	00-05-8227-106	25	Medium	Yellow	No
5	00-05-8227-90	40	Very high	Slightly yellow	No
6	00-05-8227-103	25	Medium	Slightly yellow	No
7	00-05-8227-82	40	Low	White	Yes
8	00-05-8227-87	40	High	Yellow	Turbid
8	00-05-8330-11	25	Medium	Yellow	No
9	00-05-8227-93	40	High	Slightly yellow	No
9R	00-05-8227-98	40	High	Slightly yellow	No
10	00-05-8227-107	25	Medium	Slightly yellow	No
11	00-05-8227-84	40	Very Low	Clear	No
13	00-05-8227-112	25	Low	Yellow-orange	No
13R	00-05-8330-10	20	Low	Yellow-orange	No
14	00-05-8227-109	25	Medium	Slightly yellow	No
16	00-05-8227-91	40	Very high	Slightly yellow	No
16R	00-05-8227-99	40	High	Slightly yellow	No
17	00-05-8227-110	25	Medium	Slightly yellow	No
18	00-05-8227-86	40	Very Low	Clear	No

5.0 PREPARATION OF FILMS

To prepare films of at least 0.5 mm to 3.0 mm thickness, polyurethane solutions were evaporated on glass plate molds using the following technique:

1. Six mm thick plate glass pieces were cut for the evaporation molds. Initially, mold sizes were approximately 10 cm x 20 cm but later were 20 cm x 20 cm.

2. A HDPE adhesive release film (DeWal 423-10) was applied to one side of the glass plates, keeping an approximately 1 cm border at the edge glass plate uncovered.

3. A silicone bead (GE Silicone II) was placed on the outer glass edge to build up a wall that could retain the polyurethane solution. The bead was doubled in height for more dilute solutions. For the 20 cm x 20 cm plates, a 1 cm strip of the HDPE film was removed from the plate centre and a silicone bead used to subdivide the plate into two equal halves. The silicone was allowed to cure for at least 18 hours before usage.

4. The glass plate molds were placed in forced-air, vented ovens and then leveled using a bubble level gauge and appropriate shimming. Leveling is important so that the solution maintains the same depth on the mold to give a uniform thickness in the final film.

5. A calculated amount of solution was poured onto the plate in order to give a final film thickness of about 1 mm. The calculation is based on the area on the plate, solution solids concentration and approximate polyurethane density.

6. The solutions were oven dried at 68°C over a period of about one week.

Using this method, it was possible to prepare films for most of the solutions. A brief description of the films prepared and their physical properties is given below:

As can be seen in Table V, DREA reactions 1, 1R, 13 and 13 R could not be formed into films. Instead, the films shrank and cracked as the DMF solvent evaporated. One possible explanation is that the polyurethanes are simply too brittle, as evidenced by their respective glass transition temperatures (see Table A3). The physical nature of the films (elastomeric, brittle, gooey) can be explained at least in part by the glass transition temperatures of the polyurethanes; that is, a material with a high T_g is more brittle while low T_g materials are "gooey". This effect is moderated by the amount of hard segment functionality in the polymer composition.

Table V
Properties of Polyurethane Films

DREA Reaction #	Bodycote Film Sample #	Made from Reaction Solution #	Comment on Film
1	00-05-8330-12-1	00-05-8330-7	Brittle solid, mudcracked
1R	00-05-8330-12-2	00-05-8330-8	Brittle solid, mudcracked
2	00-05-8330-24	00-05-8227-80	Mudcracked, partial film formation*
3	00-05-8227-101-1	00-05-8227-92	Gooey
4	00-05-8227-111-4	00-05-8227-106	Elastomeric solid
5	00-05-8227-108-1	00-05-8227-90	Elastomeric solid
6	00-05-8227-111-3	00-05-8227-103	Elastomeric solid
7	00-05-8227-108-4	00-05-8227-82	Opaque, brittle solid
8	00-05-8227-108-2	00-05-8227-87	Elastomeric solid
9	00-05-8227-101-2	00-05-8227-93	Elastomeric solid
9R	00-05-8227-108-3	00-05-8227-98	Elastomeric solid
10	00-05-8227-111-5	00-05-8227-107	Elastomeric solid
11	00-05-8227-111-1	00-05-8227-84	Very gooey
13	00-05-8330-09-3	00-05-8227-112	Brittle solid, mudcracked
13R	00-05-8330-15-1	00-05-8330-10	Brittle solid, mudcracked
14	00-05-8330-09-1	00-05-8227-109	Elastomeric solid
16	00-05-8227-101-3	00-05-8227-91	Gooey
16R	00-05-8227-101-4	00-05-8227-99	Gooey
17	00-05-8330-09-2	00-05-8227-110	Elastomeric solid
18	00-05-8227-111-2	00-05-8227-86	Very Gooey
8**	00-05-8330-15-2	00-05-8330-11	Elastomeric solid

* The precipitated solution was diluted to 20% and dried at 105°C overnight
** Repeat of reaction # 8 , done at lower solids content

6.0 ANALYTICAL RESULTS

6.1 GPC - DRI for Analysis for Residual Polyols/Glycols

Unreacted polyols and glycols in the polyurethane films were determined by analysis with a gel permeation chromatograph with differential refractive index detector (GPC-DRI). GPC traces and the method used are given in the attached Bodycote Ortech Report 00-04-224-8.

Tetrahydrofuran (THF) was used as a solvent for the procedure. Standards of the respective polyols and glycols were first prepared in THF and analyzed to determine detector response factors as shown below:

Table VI
GPC-DRI Polyol/Glycol Standards

Sample	Material	% w/w in THF	DRI Area Counts, μV-sec	Retention Time, Minutes	Response Factor*
00-05-8227-96-1	BDO	0.3999	3442233	29.683	1.1617×10^{-7}
00-05-8227-96-2	T650	0.3999	4354204	24.050	0.9184×10^{-7}
00-05-8227-96-3	T1000	0.3995	4098813	23.650	0.9724×10^{-7}
00-05-8227-96-4	T1400	0.4000	4208366	20.517	0.9505×10^{-7}
00-05-8227-96-5	DEG	0.4002	5345414	29.500	0.7487×10^{-7}
00-05-8227-96-6	P600	0.4001	3934398	25.083	1.0169×10^{-7}
00-05-8227-96-7	P1000	0.4000	4363174	23.667	0.9168×10^{-7}
00-05-8227-96-8	DMPD	0.4000	2928238	28.983	1.3660×10^{-7}
00-05-8227-96-9	DMF	0.4000	10264962	30.350	0.3897×10^{-7}

* Response factor = value to multiply area counts of peak by in order to get %w/w

It can be seen that DRI response factors are similar for the polyols and glycols except for DMPD. Dimethyl formamide was also examined to see if it could also be quantified by this technique, but it overlaps the solvent peak at 30.45 min.

Samples of films were dissolved in or extracted by THF to get the appropriate values of any unreacted glycols. About 0.3 grams of sample polyurethane was cut from the films and placed in 10 mL glass vials. About 10 grams of THF solvent was then added. The samples were allowed to sit overnight to dissolve or extract into the THF. The THF solutions were then analyzed by GPC and the traces are shown in Bodycote Report # 00-04-224-8 as sample traces 00-05-8330-18A to 00-05-8330-23-2.

Peak areas of the traces can be used to calculate residual wt % polyol or glycol in the original films. Unfortunately, the analysis for residuals becomes somewhat complex. In looking at the peaks seen in the polymerized materials, one must keep in mind what was added to the original formulation. For example, if only DEG was used in the original formulation, (e.g. DREA Reaction #1) then one needs only look for a DEG peak at 29.50 minutes in the DRI trace; everything higher in molecular weight will be a polymer or oligomer. Considering this, the following samples were examined and evaluated :

Table VIIA
GPC-DRI Analysis of Glycol-Only Polyurethanes

DREA rx #	THF Solution #	Observed Peak(s) RT, min	RT for Original Glycol, min	% Residual Glycols in Sample
1	00-05-8330-19C	25.517	29.50 (DEG)	ND
1R	00-05-8330-20A	22.967, 24.283, 5.767	29.50 (DEG)	ND
2	00-05-8330-23-1	22.083, 22.517, 23.05, 23.717, 24.667, 25.433, 26.133, 27.583, 28.95	28.983 (DMPD) 29.683 (BDO)	0.64%
7	00-05-8330-18B	22.517, 23.050, 23.667, 24.667, 26.217, 28.750	29.50 (DEG) 28.983 (DMPD)	ND
13	00-05-8330-20C	21.383, 21.867, 22.400, 23.117, 24.117, 25.767	29.50 (DEG)	ND
13R	00-05-8330-22-3	21.300, 21.817, 22.350, 23.050, 24.083, 25.750	29.50 (DEG)	ND

ND = not detected

For the samples where there were polyols but no glycols, any peaks in the region of 20 to 30 minutes might indicate residual polyols. The samples representative of this group are shown below:

Table VIIB
GPC-DRI Analysis of Polyol-Only Polyurethanes

DREA rx #	THF Solution #	Observed Peak(s) RT, min	RT for Original Glycol	% Residual Glycols in Sample
16	00-05-8330-21B	none	20.517 (T1400)	ND
16R	00-05-8330-21D	none	20.517 (T1400)	ND

For the remainder of the samples there is a combination of glycol and polyol in the formulations. For these it is unclear as to whether there is a residual or not, because reacted glycol/isocyanate oligomers will have a similar retention time to the unreacted polyol. Samples in this group are shown below:

Table VIIC
GPC-DRI Analysis of Polyol/Glycol Polyurethanes

DREA rx #	THF Solution #	Observed Peak(s) RT, minutes	RT for Original Polyol/Glycol	% Residual Polyols in Sample (Apparent)
3	00-05-8330-21C	23.95, 25 5	20.517 (T1400) 28.983 (DMPD)	!.05
4	00-05-8330-18D	24.317, 25.783	as above	3.45
5	00-05-8330-19B	23.933, 25.483	as above	0.69
6	00-05-8330-18A	22.283, 22.95, 24.057, 25.517	as above	3.31
8	00-05-8330-22-4	25.533	25.083 (P600) 28.983 (DMPD)	1.98
8	00-05-8330-19C	25.517	as above	1.49
9	00-05-8330-20B	24.033, 25.533	23.667 (P1000) 28.983 (DMPD)	0.93
9R	00-05-8330-18C	29.983, 25.53	as above	1.03
10	00-05-8330-19A	22.233, 22.917, 24.1, 25.5	as above	3.30
11	00-05-8330-21A	23.683, 24.633, 26.1, 28.6	as above	3.80
14	00-05-8330-22-1	22.217, 22.9, 24 017, 25.5	24.050 (T650) 28.983 (DMPD)	3.11
17	00-05-8330-22-2	22.25, 22 917, 23.933, 25 483	23.650 (T1000) 28.983 (DMPD)	3.48
18	00-05-8330-20D	23.033, 23.7, 24.633 26.1, 28.617	as above	3.17

In this case, the assumption is made that anything in the region of 20 to 30 minutes is a residual polyol and this gives the observed values, using an averaged 1.01×10^{-7} response factor and multiplying by the cumulative area of all the peaks. It is noteworthy, however, that the amount of apparent residual polyol seems related to the level of DMDP as shown in Figure A1. A linear correlation can be seen, suggesting that DMPD directly contributes to the % residual. There are two possibilities: 1) The DMPD reacts with isocyanate to form oligomers, as was noted for the other glycols, or 2) The DMPD contains water, which results in an incomplete conversion for the polyols. The former explanation seems more likely, especially because retention times of the residual peaks cannot be matched to the original polyols.

Good molecular weight traces were also obtained from the GPC for those samples that completely dissolved in THF. It is worth noting the molecular weight distributions and the molecular weights for all of these samples were similar. For the polymers which did not dissolve or did not dissolve completely, the polymer peak is much lower in molecular weight, as would be expected since only the low molecular weight fraction of the sample would dissolve.

6.2 Elemental Analysis

Samples of films were sent to Galbraith Laboratories, Inc. (Knoxville, TN 37950-1610) for elemental analysis. Carbon, nitrogen, and hydrogen content were determined by a combustion method adhering to ASTM methods D 5373/D 5291. Oxygen content was determined by a pyrolysis technique.

The results of the analysis is shown in Table A4 in Appendix A. The calculated elemental values based on the formulation composition are also included in the table. Agreement is reasonable, but some trends can be seen. The analyzed value for the oxygen is typically higher than the calculated value and hydrogen slightly higher, whereas the carbon content is lower and nitrogen is variable. This discrepancy might be explained by water absorbed into the samples. However, the fact that the cumulative elemental analysis is usually over 100% puts the results in some question. Galbraith Laboratories personnel indicated that oxygen tends to be high in analyses of certain materials, but they could not speculate whether these polyurethane samples would have this problem. Some samples were re-analyzed for oxygen content, but the results were essentially the same.

Elemental analysis results for DREA reactions numbers 1 and 1R, 9 and 9R, 13 and 13R, and 16 and 16R show good reproducibility for samples of the same formulation.

7.0 SUMMARY AND CONCLUSIONS

In this project many problems arose because of the large differences among the polyurethanes, including monomer reactivity, physical properties, solvency and other properties. This makes it impossible, or at least tricky, to use one set of reaction conditions in a "one-shot" preparation. The large variability in the physical properties of the resulting materials made it difficult to use one set of conditions for the mold/demold procedure.

Fortunately, moving to solution polymerization in DMF eliminated most of the preparation problems associated with individual reactions such that one standardized set of reaction conditions could be used. However, the final polyurethane test specimens must be prepared by solvent evaporation.

Again, physical differences among the various polyurethanes led to problems - the brittle materials could not effectively be made into films. This may be solved by using another solvent or different reaction conditions, however.

All prepared solutions and evaporated films were submitted to Defense Research Establishment Atlantic for evaluation.

Appendix A

(4 Tables, 1 Figure)

Table A1
Molar Ratios of Reactants for Polyurethane Formulations

DREA Reaction #	BDO	T650	T1000	T1400	DEG	P600	P1000	DMPD	MDI	HDI
1	1								1	
1R	1								1	
2	1							1		2
3			1					0.5	1.5	
4			1					5	6	
5				1				1	2	
6				1				5	6	
7					1			1		2
8						1		0.5	1.5	
9							1	1	2	
9R							1	1	2	
10							1	5	6	
11							1	5		6
13					1				1	
13R					1				1	
14		1						5	6	
16			1						1	
16R			1						1	
17			1					3	4	
18			1					3		4

Table A2
Mass Ratios of Reactants for the Polyurethane Formulations

DREA Reaction #	BDO	T650	T1000	T1400	DEG	P600	P1000	DMPD	MDI	HDI
1	26.478								73.522	
1R	26.478								73.522	
2	16.983							19.627		63.390
3			69.586					3.705	26.709	
4			32.597					17.357	50.046	
5				69.472				5.258	25.269	
6				40.491				15.324	44.185	
7					19 413			19.052		61.535
8						57.988		5.118	36.894	
9							61.891	6.564	31.544	
9R							61.891	6.564	31.544	
10							32.687	17.334	49.979	
11							39.094	20.731		40.175
13					29.778				70.222	
13R					29 778				70.222	
14		24.011						19.568	56.421	
16			79.625						20.375	
16R			79.625						20.375	
17			42.680					13.635	43.684	
18			49.816					15.915		34.268

Table A3
Estimated Glass Transition (T_g) and Melting Temperatures (T_m) for Polyurethane Formulations*

DREA Reaction #	Estimated T_g, °C	Estimated T_m, °C
1	67	242
1R	67	242
2	16	165
3	-32	92
4	19	170
5	-35	87
6	6	150
7	15	164
8	-3	136
9	-13	120
9R	-13	120
10	23	176
11	-16	116
13	63	237
13R	63	237
14	33	191
16	-46	70
16R	-46	70
17	5	148
18	-32	92

*Based on calculations provided by DREA.

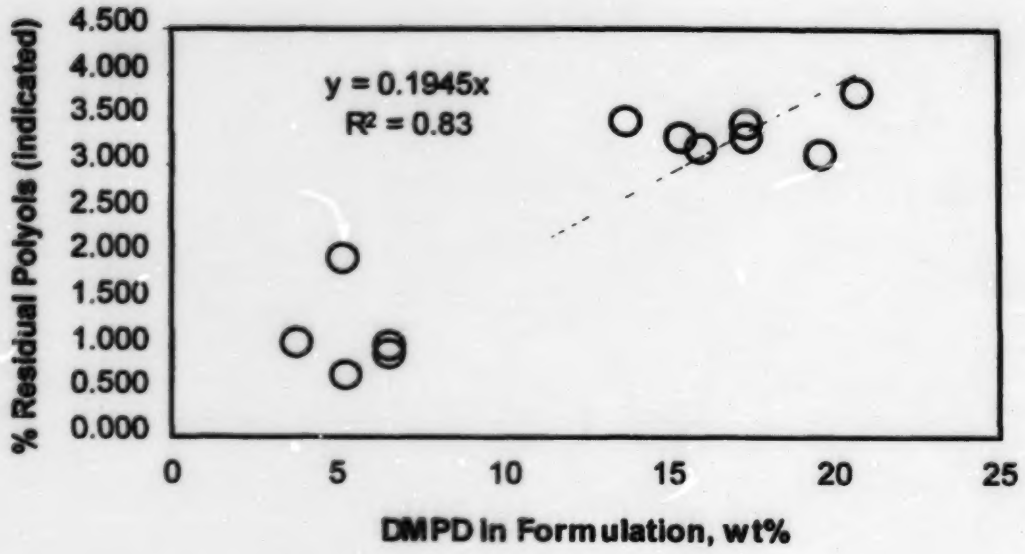

Figure A1 - % Residual Polyols (indicated) in Prepared Polyurethanes versus DMPD in Formulation Composition

Table A4
Elemental Analysis of Polyurethane Formulations

DREA #	Ortech Sample #		Carbon	Hydrogen	Nitrogen	Oxygen	Sum*
1	00-05-8330-12-1	calculated	67.05	5.92	8.23	18 80	100
		analyzed	63.68	6.59	9 90	19 44	99.61
1R	00-05-8330-12-2	calculated	67 05	5.92	8.23	18.80	100
		analyzed	63 93	6.57	9.74	18 95	99.19
2	00-05-8330-24	calculated	56.59	8.74	10 56	24.12	100
		analyzed	55 55	9.31	11.06	26.44	102 36
3	00-05-8227-101-1	calculated	66.88	9.29	2.99	20.85	100
		analyzed	66.20	9.47	2 89	23.03	101.59
4	00-05-8227-111-4	calculated	67.36	7.68	5.60	19.36	100
		analyzed	65 78	8.00	6.25	19 36	99 39
5	00-05-8227-108-1	calculated	66 91	9.40	2 83	20 87	100
		analyzed	66 34	9 77	2 71	23.05	101 87
6	00-05-8227-111-3	calculated	67 27	8 09	4 94	19 70	100
		analyzed	66 04	8 45	5.32	19 82	99 63
7	00-05-8227-108-4	calculated	54 93	8 48	10 25	26 34	100
		analyzed	54 28	8.98	10 65	28 71	102 62
8	00-05-8227-108-2	calculated	60.16	7.42	4 13	28.29	100
		analyzed	59.63	7.62	4.01	31 77	103.03
9	00-05-8227-101-2	calculated	59.63	7 72	3.53	29 12	100
		analyzed	58 50	7.78	3 36	32.86	102 50
9R	00-05-8227-108-3	calculated	59.63	7 72	3.53	29 12	100
		analyzed	58 94	7 98	3.36	32 20	102.48
10	00-05-8227-111-5	calculated	63 48	7 03	5 60	23 90	100
		analyzed	61 79	7 26	6 12	25.99	101.16
11	00-05-8227-111-1	calculated	55 83	8 89	6 69	28 59	100
		analyzed	54 73	9.42	6 40	32.30	102.85
13	00-05-8330-09-3	calculated	64 04	5.66	7 86	22 45	100
		analyzed	62 33	6 02	8.62	24 87	101.84
13R	00-05-8330-15-1	calculated	64 04	5 66	7.86	22 45	100
		analyzed	62 39	6.08	8.59	24.68	101 74
14	00-05-8330-09-1	calculated	67 45	7.23	6.31	19 01	100
		analyzed	64.81	7 83	7 54	19.41	99.59
16	00-05-8227-101-3	calculated	66 75	9.73	2 28	21.25	100
		analyzed	66 02	10.14	2 16	23 68	102.00
16R	00-05-8227-101-4	calculated	66.75	9.73	2 28	21.25	100
		analyzed	66 15	10.17	2 14	23.47	101 93
17	00-05-8330-09-2	calculated	67.23	8.12	4 89	19.77	100
		analyzed	66 02	8.44	5 05	19 77	99 28
18	00-05-8227-111-2	calculated	61.34	9.89	5.70	23.07	100
		analyzed	60 77	10 43	5 44	25 44	102 80

* Sum = % C + %H + %N + %O

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The use of Group Contribution Analysis (GCA) and Group Interaction Modelling (GIM) to model the dynamic mechanical properties of polymers is the subject of an ongoing TTCP (The Technical Cooperation Panel) study. This report describes the synthesis of 20 phase mixed thermoplastic polyurethanes that will be characterized and modelled by GCA and GIM The polyurethane formulations were synthesized from 4,4'-methylenebis(phenyl isocyanate) or 1,6-diisocyanatohexane, and glycol, polgylcol, or glycol/polyglycol mixtures. The standard "one-shot" batch reaction method was initially tried for several of the formulations, but a number of problems were identified. These included bubble formation in the samples, high exotherms, and fast reaction times. As a result, a solution polymerization/ solution casting method was developed, using N,N-dimethylformamide as a solvent. This approach has several advantages including control of the reaction temperature and rate and the absence of bubble formation in the samples. All 20 of the formulations were successfully prepared in solution, and 15 of the formulations were successfully solvent cast into 1 mm thick film samples for DMTA testing. Five of the samples did not form satisfactory films on solvent evaporation, as a result of cracking or non-uniform geometries that developed during the drying process. Gel permeation chromatography experiments revealed the presence of 1- 3% low molecular weight species which was attributed to oligomer content in polyurethanes prepared from 2,2-dimethyl-1,3-propanediol chain extender. Elemental analysis results were on average within 1.32%, 0 40%, 0.50%, and 1.91% of their expected values for carbon, hydrogen, nitrogen, and oxygen, respectively.

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